SPECIFICATION

[Title of the Invention]

Anode Thin Film for Lithium Secondary Battery and Preparation Method thereof

[Brief Description of the Drawings]

FIG. 1 is an X-ray diffraction analysis of tin-nickel powders prepared in Example 1 according to the present invention using mechanical milling and heating;

FIG. 2 is cycle characteristics of tin-nickel powders prepared in Example 1 according to the present invention using mechanical milling and heating;

FIG. 3 is an X-ray diffraction analysis showing the structural change of Ni_3Sn_4 powders prepared in Example 1 of the present invention during the electrochemical intercalation/deintercalation of lithium;

FIG. 4 is an X-ray diffraction analysis of tin-nickel thin films prepared using e-beam evaporation and ion beam assisted deposition (IBAD) of Ni_3Sn_4 powders used as an evaporation source according to Example 2 of the present invention;

FIG. 5 is a graph showing the cycle characteristics of anodes using tin-nickel thin films prepared using e-beam evaporation and IBAD of Ni_3Sn_4 powders used as an evaporation source according to Example 2 of the present invention;

FIG. 6 is an X-ray diffraction analysis of tin-nickel thin films prepared through simultaneous bombardment of e-beam onto tin (Sn) and nickel (Ni) used as evaporation sources according to Example 2 of the present invention;

FIG. 7 is a graph showing the cycle characteristics of anodes using tin-nickel thin films prepared through simultaneous bombardment of e-beam onto tin (Sn) and nickel (Ni) used as evaporation sources according to Example 2 of the present invention;

FIG. 8 is a graph showing the cycle characteristics of zirconium-containing tin single films prepared in Example 3 of the present invention with respect to a zirconium composition; and

FIG. 9 is a graph showing the cycle characteristics with thickness of $Sn_{0.5}Zr_{0.5}$ single films prepared in Example 3 of the present invention.

[Detailed Description of the Invention]

[Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to an anode thin film for a lithium secondary battery and a preparation method thereof. More particularly, the present invention relates to an anode thin film for a lithium secondary battery using tin (Sn) and nickel (Ni) as a material of forming an anode active material layer formed on a current collector and thus having improved charging/discharging cycle characteristics.

It is known that metallic lithium in an organic electrolyte is thermodynamically unstable and is coated with a thin surface layer called a solid electrolyte interface (SEI). The instability of the metallic lithium leads to deterioration of cycle efficiency when the metallic lithium is used as an electrode and powdery or dendrite growth during the repetition of charging and discharging, resulting in deterioration in stability of battery. A lithium ion battery can maintain its stability and high capacitance characteristics by employing graphite, instead of metallic lithium, as an anode material. A graphite anode enables reversible storage and separation of lithium through intercalation and deintercalation of lithium ions. Since the stored lithium ions are not in a metallic form, factors that may adversely affect the stability of a battery, for example, dendritic growth, can be removed. However, the energy density (372 mAh/g) of a graphite anode is only approximately 10% of that (3,860 mAh/g) of a metallic lithium anode. To solve the problem of small energy density, there have been proposed various anode materials exhibiting improved capacity relative to graphite, including disordered carbonaceous materials, nitrides, and oxides.

Oxide-based anodes, typically tin oxide-based anodes, which were first introduced by Fuji Photo Film Co., Ltd. (Japan) in 1996, have approximately twice a charge/discharge capacity of graphite-based anodes and are excellent in potential characteristics compared with existing substitutes. Therefore, various studies about oxide-based anodes have been extensively done. Oxide-based anodes are composed

4

of oxides of metal that can form lithium alloys, such as tin oxide (SnO or SnO_2), lead oxide (PbO), or silicon oxide (SiO). These oxide-based anode materials serve as precursors of anode active materials. Therefore, oxygen ions and metal ions are separated from each other by diffusion of lithium ions in a metal oxide lattice. Intercalated lithium ions react with oxygen ions and thus metal separation occurs in the metal oxide lattice. Active materials capable of charging/discharging are substantially metals separated in the above-described manner. For example, in tin oxides, it is known that lithium can be stored/removed by an alloying reaction between tin and lithium.

The oxide-based anode materials such as tin oxides have good cycle characteristics, compared with lithium alloys, in the following two reasons. First, a metal capable of forming lithium alloy, e.g., tin, which is separated by lattice diffusion of lithium ions, is very small in size, and thus, the mechanical loss of an active material by a volumetric change of the metal can be minimized. Second, since lithium oxide (Li_2O), produced by the reaction between lithium ions and oxygen ions simultaneously with metal separation during initial storage of lithium, serves as a buffer for a change in volume, and the separated metal and the lithium oxide (Li_2O) are uniformly dispersed, damage to the active material due to a change in volume can be prevented. However, the oxide-based anodes exhibit a relatively high initial irreversible capacity due to formation of lithium oxide, which is inevitably generated during the first charging/discharging cycle. Accordingly, an excess amount of a cathode active material is required, which is impediment to practical use.

In order to reduce the initial irreversible capacity while maintaining high capacity and good cycle characteristics of an oxide-based anode, the use of an intermetallic compound or nano-sized metal powder has been proposed. An intermetallic compound for an anode of a lithium ion battery, for example, Sn_2Fe or Cu_6Sn_5, is composed of a metal which does not form a lithium alloy and a metal which is reactive with lithium. Since the intermetallic compound does not undergo irreversible reaction by lattice diffusion of lithium ions, e.g., Li_2O formation reaction, unlike an oxide-based anode

5

material, initial irreversible capacity can be reduced. However, a tin-based intermetallic compound causes aggregation of tin due to repeated intercalation/deintercalation of lithium ions, which aggravates a mechanical damage to an active material by a change in volume, like metallic tin, resulting in considerable deterioration of cycle characteristics.

To solve the above-described problems, Mao et al. made an attempt to use a composite material composed of an active-phase material enabling intercalation/deintercalation of lithium and an inactive-phase material unreactive with lithium, prepared by a mechanical alloying method, as an anode material. Generally, a composite material prepared by a mechanical alloying method has a uniform ultrafine grain structure. A composite material composed of Sn_2Fe (active-phase material) and $SnFe_3C$ (inactive-phase material) proposed by Mao et al. also has a uniform ultrafine grain structure, and exhibits improved cycle characteristics in spite of reduction in energy density due to addition of the inactive-phase material. However, there is a problem in that due to the presence of the inactive-phase, an energy density per volume is large but an energy density per weight is very small as less than 200 mAh/g.

[Technical Goal of the Invention]

In view of the above-described problems, the present invention provides an anode thin film for a lithium secondary battery which is improved in charging/discharging characteristics and a method of forming the same.

[Structure and Operation of the Invention]

To accomplish the above objects, there is provided an anode thin film for a lithium secondary battery including a current collector and an anode active material layer formed thereon, wherein the anode active material layer contains an intermetallic compound of tin (Sn) and nickel (Ni). Preferably, the intermetallic compound is Ni_3Sn_4.

According to another aspect of the present invention, there is provided an anode thin film for a lithium secondary battery including a current collector and an anode active

material layer formed thereon, wherein the anode active material layer is a single layer containing tin (Sn) and a metal selected from zirconium (Zr), vanadium (V), manganese (Mn), titanium (Ti), nickel (Ni), and copper (Cu).

A lithium-tin alloy electrode has a relatively low operating voltage, i.e., 0-0.7 V or less, with respect to a lithium electrode. An anode made of lithium-tin alloy ($Li_{4.4}Sn$) has an energy density of 790 mAh/g, which is higher than that made of a lithium-graphite compound (LiC_6) having an energy density of 342 mAh/g. However, in lithium-tin alloy enabling intercalation/deintercalation of lithium, aggregation of tin, which is due to intercalation/deintercalation of lithium, and a severe change in volume of aggregated tin, cause cracks on the surface of and within tin, which leads to electrical disconnection with a current collector, thereby deteriorating cycle characteristics. The present invention is directed to improvement in cycle characteristics by improving structural stability by use of an intermetallic compound of tin and nickel in order to solve an inherent problem of tin, that is, in order to suppress a stress due to volumetric expansion of tin.

Unlike the conventional lithium-tin alloy, the intermetallic compound (Ni_3Sn_4) of nickel and tin is an intermetallic compound composed of tin which is an active material reacting with lithium and nickel which does not react with lithium. The Ni_3Sn_4 intermetallic compound does not undergo a compound-forming reaction with lithium ions diffused into the Ni_3Sn_4 lattice, thereby leading to a very small initial irreversible capacity, unlike oxygen ions of an oxide-based anode material. The Ni_3Sn_4 intermetallic compound is synthesized by a mechanical alloying method using tin and nickel powders. A method of forming a thin film made of the Ni_3Sn_4 intermetallic compound is not particularly limited. However, in the present invention, there are used e-beam evaporation and ion beam assisted deposition (IBAD) using simultaneous bombardment of e-beam onto tin and nickel used as evaporation sources. At this time, the tin and nickel evaporation sources directing toward a substrate are treated with accelerated argon (Ar) ions to increase the mobility of the evaporation atoms or to modify the surface state of a tin-nickel thin film. The composition of the tin-nickel thin film can be

changed by adjusting the electron flux of e-beam. The crystallinity and fine structure of the tin-nickel thin film can be adjusted by changing the flux and acceleration voltage of Ar ions.

The present invention is also directed to solution of an inherent problem of tin, i.e., reduction in a stress due to volumetric expansion of tin, and control of a lithium-tin reaction and enhancement of structural stability by maintaining a binding between tin and its counter metal during intercalation of lithium, thereby improving cycle characteristics. Here, the counter metal is required to have good ductility and toughness and strong chemical affinity with tin. That is, the reaction enthalpy between tin and the counter metal must be negative, i.e., $\Delta H(Sn-M) < 0$. A metal capable of forming a tin-metal bond during intercalation/deintercalation of lithium may be zirconium, vanadium, manganese, titanium, nickel, or copper. In particular, zirconium has a strong chemical affinity with tin, and thus, controls a tin-lithium reaction during lithium intercalation and provides structural stability during repeated intercalation/deintercalation of lithium.

An anode thin film according to the present invention includes an anode active material layer in which tin is dispersed in a base made of a metal selected from zirconium, vanadium, manganese, titanium, nickel, and copper by a thin film deposition process. A method of forming a tin-metal containing single layer is not particularly limited but co-sputtering of tin and a metal selected from zirconium, vanadium, manganese, titanium, nickel, and copper is used in the present invention. When tin is deposited simultaneously with a metal selected from zirconium, vanadium, manganese, titanium, nickel, and copper by sputtering, tin is dispersed to a size of several tens of nanometers or less in the metal base to thereby form a tin-metal single thin layer. In the formation of a tin-metal single layer by co-sputtering, the characteristics of a finally obtained anode active material layer may slightly vary according to the distribution state, particle size, and mixture ratio of the metal. However, since the metal can be controlled to be uniformly distributed in a fine particle state between tin particles, good cycle characteristics can be obtained.

Preferably, in the tin-metal single layer, the molar ratio of the tin and the metal is in the range of 7.5:2.5 to 5:5. If the ratio of the metal to the tin exceeds 5 to 5, fine tin particles, which are active materials reacting with lithium, may be shielded by metal atoms, which prevents the reaction between tin and lithium, thereby leading to a

5   substantially reduced electrode capacity, as compared with a designed electrode capacity. On the other hand, if the ratio of the metal to the tin is less than 2.5 to 7.5, the reaction between lithium and tin may increase. As a result, a prevention effect of volumetric change of tin particles may be insufficient. The thickness of the tin-metal single layer can be diversely changed according to the requirements of a device and the

10   capacity of a cathode. However, it is preferable to adjust the thickness of the tin-metal single layer to less than 1,500□. If the thickness of the tin-metal single layer exceeds 1,500□, the reaction between lithium and tin may increase, which renders sufficient reduction of stress due to volumetric expansion and contraction of tin difficult.

An anode thin film according to the present invention may also include, as an

15   anode active material layer, a single layer containing a metal selected from zirconium, vanadium, manganese, titanium, nickel, and copper; tin; and silver (Ag). When the above-described tin-metal single layer is used for an anode thin film, as described above, there may arise a problem that fine tin particles may not react with lithium when they are surrounded by metal particles not reacting with lithium. In this respect, use of

20   silver with ionic conductivity for lithium ions can solve the problem of no reaction between tin and lithium when tin particles are surrounded by metal particles, thereby increasing the capacity of an anode material. A method of forming a tin-silver-metal single layer is not particularly limited. However, co-sputtering of a metal selected from zirconium, vanadium, manganese, titanium, nickel, and copper; tin; and silver is used in

25   the present invention. In the formation of a tin-silver-metal single layer by co-sputtering, the characteristics of a finally obtained anode active material layer may slightly vary according the distribution state, particle size, and mixture ratio of silver and metal particles in tin particles. However, since the silver and metal particles can be controlled

to be finely and uniformly distributed between the tin particles, an anode thin film with good cycle characteristics can be formed.

The present invention will now be described in more detail through the following Examples, but not limited thereto.

Example 1

Tin (Sn) and nickel (Ni) powders were mixed in a molar ratio of 4:3 to prepare Ni_3Sn_4 powders by the following mechanical alloying method. That is, tin and nickel powders were weighed in a molar ratio of 4:3, mixed sufficiently using an agate mortar, and ball-milled at about 750 rpm using an oscillation-type ball mill for about 10 hours. After ball-milling, the resultants were heated at 350□ and 500□ for about one hour. The X-ray diffraction (XRD) analysis results are shown in FIG. 1. From (a) of FIG. 1, it can be seen that the tin and nickel powders used as starting materials disappeared and only Ni_3Sn_4 was prepared by a mechanical alloying method using the mechanical milling of the mixture of the tin and nickel powders for about 10 hours. As shown in (b) and (c) of FIG. 1, the Ni_3Sn_4 crystallinity increased as the heating temperature increased to 350□ and 500□. In order to evaluate electrochemical properties of the Ni_3Sn_4 powders prepared by the above-described procedure, lithium secondary batteries were fabricated using metallic lithium as a counter electrode and a reference electrode and using a solution of 1 M $LiPF_6$ in a mixed solvent of ethylene carbonate (EC) and diethylcarbonate (DEC) as an electrolyte solution. The cycle characteristics of the fabricated lithium secondary batteries are shown in FIG. 2. Here, the cycle characteristics were evaluated by performing charging and discharging of lithium at a constant current density of 0.2 mA/cm^2 within the range of measured potential of 0 to 1.2 V. Referring to FIG. 2, as the Ni_3Sn_4 crystalinity became better, the charging/discharging capacity was reduced but cycle characteristics were remarkably enhanced. Also, the charge/discharge capacity of the Ni_3Sn_4 powders was proportionate to a volume fraction of the grain boundary of the powders depending on the heat treatment performed after milling. The Ni_3Sn_4 powders with good crystalinity did not exhibit a decrease in capacity even during repeated intercalation/deintercalation

of lithium, from which lithium is presumably intercalated/deintercalated into/from the grain boundary of the Ni_3Sn_4 powders. Here, grains of Ni_3Sn_4 unreactive with lithium act as hosts for lithium intercalation, which suppresses volumetric expansion, thereby maintaining good cycle characteristics.

FIG. 3 is an XRD analysis showing structural change of Ni_3Sn_4 powders prepared by milling tin and nickel powders for about 10 hours and then heating the same at 500□ for about 1 hour, during electrochemical intercalation/deintercalation of lithium into/from the Ni_3Sn_4 powders. Referring to FIG. 3, when lithium intercalation was performed at an initial state (a) until a charging voltage reached 0.05 V (c) and then lithium deintercalation was performed until a discharging voltage reached 1.2 V (d), the Ni_3Sn_4 crystalinity was still maintained. Even after 100 cycles of these procedure (e), no change in the diffraction pattern was observed. In tin-based intermetallic compounds that have been reported so far, a phase change occurs during lithium intercalation. Therefore, tin and its counter metal are separated by diffusion of lithium ions and the lithium ions react with the tin to form a lithium-tin (Li-Sn) alloy phase. The lithium-tin alloy phase thus formed has very small particle size and is uniformly distributed, thereby exhibiting improved cycle characteristics relative to metallic tin. However, such a tin-based intermetallic compound undergoes aggregation of tin due to repeated intercalation and deintercalation of lithium ions, causing severe mechanical damage to active materials due to a change in volume, like metallic tin, thereby degrading cycle characteristics. On the other hand, in the Ni_3Sn_4 structure of the present invention as shown in FIG. 3, a peak corresponding to tin was not observed during intercalation of lithium. This shows that no phase change occurs and the Ni_3Sn_4 crystal structure is maintained, unlike conventional tin-based intermetallic compounds, thereby greatly improving cycle characteristics.

As shown in FIG. 2, the Ni_3Sn_4 intermetallic compound has a capacity per weight of about 100 mAh/g, which is not suitable to be employed as an anode active material of a bulk-type battery. However, since the Ni_3Sn_4 intermetallic compound has a large density, i.e., 8.42 g/cm^3, the good cycle characteristics of the Ni_3Sn_4 intermetallic

11

compound encourages the Ni_3Sn_4 intermetallic compound to be suitably used as an anode active material for a thin film battery in which a capacity per volume is quite an important factor. Also, as shown in FIG. 3, since a change in lattice constant due to lithium intercalation/deintercalation is very small, it is presumed that a change in volume is not so big during lithium intercalation, and thus, the Ni_3Sn_4 intermetallic compound can be very suitably used as an anode material of a thin film battery requiring high mechanical stability between an electrode and an electrolyte and between an electrode and a current collector.

Example 2

Ni_3Sn_4 thin films were deposited by e-beam evaporation and ion beam assisted deposition (IBAD) using the Ni_3Sn_4 powders prepared in Example 1 as an evaporation source. FIG. 4 shows XRD analysis results of the Ni_3Sn_4 thin films deposited using the e-beam evaporation and IBAD. Referring to FIG. 4, when the duration of e-beam evaporation increased or ion beams were irradiated onto a substrate, a diffraction peak was observed around a diffraction angle of 30°, which is presumably derived from NiSn which is a metastable phase. FIG. 5 shows charging/discharging cycle characteristics of anodes using the Ni_3Sn_4 thin films prepared by the above-described process. Referring to FIG. 5, the Ni_3Sn_4 thin films with good crystallinity exhibited enhanced cycle characteristics but the cycle characteristics of the Ni_3Sn_4 thin films were not so good as those of the Ni_3Sn_4 powders with good crystallinity shown in FIG. 2. These results show that use of stoichiometrical Ni_3Sn_4 powders as an evaporation source makes it difficult to control the composition of deposited thin films. On the other hand, the IBAD process can increase the mobility and reactivity of atoms to be deposited onto a substrate by collision of accelerated ion beams with the atoms. In this regard, appropriate adjustment of ion beam conditions enables preparation of crystalline thin films even at room temperature, as shown in (c) of FIG. 4.

To solve the difficulty in controlling the composition of thin films by the use of stoichiometrical Ni_3Sn_4 powders as an evaporation source, there has been made an attempt to facilitate control of the compositions of tin and nickel through simultaneous

bombardment of e-beam onto tin and nickel used as evaporation sources. Here, accelerated argon (Ar) ions can be irradiated onto a substrate simultaneously with the Sn and Ni evaporation sources to increase the mobility of the deposition atoms or modify the surface state of thin films. The composition of thin films can be changed by adjusting the electron flux of e-beam. The crystallinity and fine structure of the thin films can be adjusted by varying the flux and acceleration voltage of Ar ions. XRD analysis results of thin films deposited by applying e-beam current of 110 mA and 75 mA to tin and nickel, respectively are shown in FIG. 6. At this time the thickness of the thin films was 950□. Referring to (b) of FIG. 6, the thin films were considered to be Ni_3Sn_2 thin films. For comparison, the XRD analysis result for a Si/SiO_2 substrate is shown in (a) of FIG. 6. The charging/discharging cycle characteristics of anodes using the Ni_3Sn_2 thin films prepared by the above-described process are shown in FIG. 7. Here, the cycle characteristics were evaluated by performing charging and discharging of lithium at a constant current of 30 $\mu A/cm^2$ within the range of measured potential of 0 to 1.2 V. As shown in FIG. 7, the anodes using the Ni_3Sn_2 thin films exhibit very low capacity because they have very low electrochemical activity. However, as described above, since the composition, crystallinity, and fine structure of thin films can be controlled by adjusting the electron flux of e-beam and the flux and acceleration voltage of Ar ions, Ni_3Sn_4 thin films can be deposited at room temperature.

Example 3

As described above, to solve an inherent problem of tin, i.e., to decrease stress due to the volumetric expansion of tin, and to control a lithium-tin reaction and enhance structural stability by maintaining a tin-zirconium (Sn-Zr) bond during intercalation of lithium, thereby improving cycle characteristics, Sn-Zr single thin films were prepared. In detail, anode thin films, which had the same structures as shown in (a) of FIG. 1 and were different in zirconium composition, were formed on copper (Cu) substrates using tin and zirconium targets (2 inches in diameter). Deposition was performed by co-sputtering of the tin and zirconium targets under the conditions of an initial vacuum state of 2×10^{-6} torr or less, an argon gas pressure of 5 mTorr, and a flow rate of 10

sccm. At this time, anode thin films different in the composition of tin and zirconium were prepared by varying the radio frequency (rf) power applied to the zirconium target within the range of 0 to 100 W while applying a constant rf power of 150 W to the tin target. To evaluate electrochemical properties of the anode thin films prepared by the

5 above-described procedure, lithium secondary batteries were fabricated using metallic lithium as a counter electrode and a reference electrode and using a solution of 1 M $LiPF_6$ in a mixed solvent of ethylene carbonate (EC) and diethylcarbonate (DEC) as an electrolyte solution. The cycle characteristics of the anode thin films different in zirconium composition relative to tin are shown in FIG. 8. Here, the cycle

10 characteristics were evaluated by performing repetitions of 100 or more of charging and discharging of lithium at a constant current density of 0.2 mA/cm^2 within the range of measured potential of 0 to 1.2 V. Referring to FIG. 8, as the addition amount of zirconium increased, battery capacity was decreased. As described above, this is because tin particles used as an active material reacting with lithium are surrounded by

15 zirconium particles, thereby reducing lithium-tin reactivity. When the addition amount of zirconium was 0.25 (molar ratio) or less, reduction in stress due to the volumetric expansion and contraction by lithium-tin reaction was insufficient, like in FIG. 2. When the addition amount of zirconium reached more than 0.25, cycle characteristics were remarkably enhanced, relative to tin single films. In particular, the anode thin films with

20 a zirconium content of 0.5 maintained 95% or more of an initial capacity even after 100 cycles. This is because zirconium particles maintain a strong binding with tin while maintaining an amorphous structure during intercalation/deintercalation of lithium. In this way, use of an anode active material layer in which fine zirconium particles are distributed about tin particles by co-sputtering can remarkably reduce deterioration of

25 the active material due to the volumetric expansion and contraction of the tin particles, thereby enhancing cycle characteristics, as compared with an anode active material layer made of pure tin. Meanwhile, the cycle characteristics with thickness of $Sn_{0.5}Zr_{0.5}$ single films were evaluated and the results are shown in FIG. 9. For this, anode thin films with the composition of $Sn_{0.5}Zr_{0.5}$ were prepared to a thickness of 300 to 1,500□

by co-sputtering of tin and zirconium at the rf power of 150 W and 100 W, respectively. Referring to FIG. 9, the tin-zirconium single thin films exhibited good charging/discharging characteristics even at a thickness of 1,100□. However, when the thickness of the single thin films was 1,500□ or more, capacity reduction with the repetition of charging and discharging was remarkably increased. As described above, this is because as the thickness of a tin-zirconium single thin film increases, lithium-tin reaction increases, and thus, zirconium cannot sufficiently reduce stress due to the volumetric expansion and contraction of tin.

[Effect of the Invention]

An anode thin film according to the present invention can suppress the volumetric expansion and contraction of tin during a charging/discharging process, thereby remarkably improving cycle characteristics. Therefore, use of the anode thin film can greatly improve the chemical and mechanical stability of the interface between an electrode and an electrolyte, which makes it possible to fabricate a lithium secondary battery with improved lifetime characteristics.

15